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IDENTIFICATION OF METAL ION CHLORO COMPLEXES IN AN
AMBIENT TEMPERATURE MOLTEN SALT.

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PROJECT 2303

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

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AIR FORCE SYSTEMS COMMAND

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The chloro complexation of $LiCl$, $AgCl$, $CdCl_2$, and $ZnCl_2$ in a chloride ion rich ambient temperature chloroaluminate ionic liquid has been studied by nuclear magnetic resonance spectroscopy. Chloride ion reacts with added metal chloride salts according to $xCl^- + MCl_m \rightleftharpoons MCl_{m+x}^{x-}$, where x is a small, positive integer. The proton chemical shift of the organic component of the molten salt is very sensitive to the free chloride concentration of the melt. Therefore, observing the change in the chemical shifts of the organic cation with increasing amounts of added metal chloride salt allows the determination of the value of x. Results indicate the formation of $LiCl_2^-$, $AgCl_2^-$, $CdCl_4^{2-}$, and $ZnCl_4^{2-}$ at 30°C. In addition, an extended model for ion interactions in these melts is described.

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IDENTIFICATION OF METAL ION CHLORO COMPLEXES IN
AMBIENT TEMPERATURE CHLOROALUMINATE MOLTEN SALTS

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January 1985

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SUMMARY

The chloro complexation of LiCl, AgCl, $CdCl_2$, and $ZnCl_2$ in a chloride ion rich ambient temperature chloroaluminate ionic liquid has been studied by nuclear magnetic resonance spectroscopy. Chloride ion reacts with added metal chloride salts according to $xCl^- + MCl_m \rightleftharpoons MCl_{m+x}^{x-}$, where x is a small, positive integer. The proton chemical shift of the organic component of the molten salt is very sensitive to the free chloride concentration of the melt. Therefore, observing the change in the chemical shifts of the organic cation with increasing amounts of added metal chloride salt allows the determination of the value of x. Results indicate the formation of $LiCl_2^-$, $AgCl_2^-$, $CdCl_4^{2-}$, and $ZnCl_4^{2-}$ at 30 °C. In addition, an extended model for ion interactions in these melts is described.

PREFACE

This report describes work performed under FJSRL Work Unit 2303-F2-10,
Organic and Inorganic Electrochemical Measurements. Dr. Reynolds is a
University Resident Research Professor at FJSRL. Dr. Scheffler is a National
Research Council postdoctral research associate at FJSRL. Dr. Wilkes is a
permanent staff member at FJSRL.

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Introduction

Low melting salts composed of mixtures of 1-methyl-3-ethylimidazolium chloride and aluminum chloride are exploitable as electrolytes for voltaic cells.[1-3] Except for simple concentration cells, most cells that use these room temperature melts will require that a redox couple be added to the melt. Numerous such couples have been studied in the 1-methyl-3-ethylimidazolium and the closely related 1-butylpyridinium chloroaluminate melts. It is clear that almost all dissolved metal ions are complexed in some manner by the melts, and that this complexation greatly affects the electrochemistry of the metal/metal ion couple. Several different methods have been applied to the determination of the nature of these metal ion complexes.[4] In the basic melts, where there is a high chloride activity, most metal ions form chloro complexes.

Since there is no uncharged solvent in these low temperature ionic liquids, extensive interionic interactions occur. We observed earlier that the ^1H and ^{13}C nuclear magnetic resonance chemical shifts of nuclei in the organic cation of melts were affected by the melt composition.[5] On a molecular scale, the shifts were related to the nature and relative amount of the different anions present in the melt. Metal chloride salts (MCl_m) added to the basic melts are usually converted to anionic chloro complexes (MCl_{m+x}^{x-}) (Eq. 1)

$$xCl^- + MCl_m \leftrightharpoons MCl_{m+x}^{x-} \tag{1}$$

and could have an influence on the chemical shifts of the nuclei in the cations. We report here that the nmr shifts of nuclei in the cations of 1-methyl-3-ethylimidazolium chloroaluminate melts are sensitive to the addition of metal ions, and that this phenomenon may be used to determine the stoichiometry of the chloride complexation in the basic melts.

Experimental

All experimental manipulations including melt synthesis and sample loading were performed inside the previously described dry box system.[6] Binary melts based on 1-methyl-3-ethylimidazolium chloride and aluminum chloride were prepared as described previously.[6] The metal chloride salts used in this study (LiCl, AgCl, $CdCl_2$, $ZnCl_2$,) were of at least reagent grade purity.

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If a salt sample had been stored outside of the dry box for any length of time, it was dried (> 100 °C, in vacuo) overnight. Binary melts based on 1-methyl-3-ethylimidazolium chloride and the various metal chloride salts were synthesized by mixing appropriate amounts of each salt in an open vessel inside the dry box. Nuclear magnetic resonance spectra were obtained using a JEOL FX90Q spectrometer equipped with a variable temperature, tunable probe. Spectra were recorded at 30 °C.

Results and Discussion

The quantitative explantation for the proton chemical shift dependences on melt composition is that the shifts are actually population weighted averages of more than one magnetic environment. Earlier work showed that three different magnetic environments were required to explain the chemical shift data, so a model was proposed where each imidazolium cation interacted with two anions and vice versa.[5] That arrangement is shown in Figure 1, with the numbers 2, 5, and 8 identifying the environments according to the total number of chloride ions in the anions.
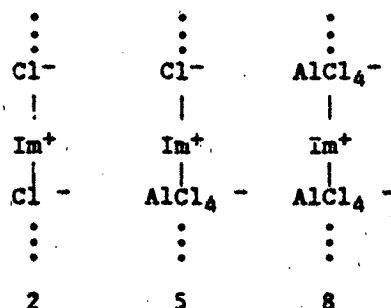
$$
\begin{array}{ccc}
\vdots & \vdots & \vdots \\
Cl^- & Cl^- & AlCl_4^- \\
| & | & | \\
Im^+ & Im^+ & Im^+ \\
| & | & | \\
Cl^- & AlCl_4^- & AlCl_4^- \\
\vdots & \vdots & \vdots \\
2 & 5 & 8
\end{array}
$$

Fig. 1   Ion interactions proposed for MeEtImCl-AlCl$_3$ binary melts.[5]

The addition of a metal ion that consumes chloride from the melt will at the very least change the proportions of the environments 2, 5 and 8. Also, the metal ion chloro complex itself may affect the shifts of the nuclei in the imidazolium cations. We have measured the effect of several metal ions by adding increasing amounts of the neutral metal chloride salt to melts of known composition (and thus known chloride fraction). In all cases we observed that the chemical shift of the proton attached to the 2 position in the imidazolium ring was the most sensitive to the amount of metal chloride salt added. We can explain this behavior by proposing ion-ion interaction models similar to Figure 1, then testing the models with the chemical shift (δ) vs mole

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fraction metal ion ($\underline{N}_M$) data. We have applied this to Li(I), Zn(II), Ag(I), and Cd(II).

The models used to interpret the data differ in the assumptions made about the nature of the ion-ion interactions and the assumptions made about which interactions may be regarded as negligible. All of the models contain the stoichiometry of Equation 1, and thus chemical shift data can provide the identity of the chloro complex formed if the model is shown to be correct by reasonable fits to the data. We have evaluated the six models discussed below.

MODEL I.

The simplest model is one where the sole effect of the added metal chloride salt is to deplete chloride ion from the melt according to the stoichiometry of Equation 1, and where the resulting chloro complex itself has no effect on the magnetic environment of the imidazolium cation. The change in chemical shift would result entirely from the change in relative fractions of 2, 5 and 8. The lack of contribution to the overall shift by the metal chloride complex may be an unwarranted assumption, but may be a reasonable approximation at low concentrations of MCl_m. Also, since this is a rather simple model, it is useful in establishing the mathematical relationships used in more complicated models.

All of the models are based on the assumption that the cations are in fast exchange on the nmr time scale. Thus the chemical shift may be expressed as a population weighted average of the different environments:

$$\delta_{obs} = \sum_{i=1}^{n} \delta_i \underline{X}_i \qquad (2)$$

where δ_i's are the shifts of the imidazolium cations in the different environments and $\underline{X}_i$'s are the fractions of each environment. In the case of model I there are three imidazolium environments, as shown in Figure 1. Equation 2 becomes

$$\delta_{obs} = \delta_2 \underline{X}_2 + \delta_5 \underline{X}_5 + \delta_8 \underline{X}_8 \qquad (3)$$

As shown earlier,[3] $\underline{X}_2$, $\underline{X}_5$ and $\underline{X}_8$ are defined as

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$$\frac{X}{2} = Y_1^2 \ , \quad \frac{X}{5} = 2Y_1Y_4 \ , \quad \frac{X}{8} = Y_4^2$$

where Y_1 and Y_4 are the anion fractions of Cl^- and $AlCl_4^-$ respectively.

In the binary MeEtImCl-AlCl$_3$ melts, Y_1 and Y_4 are rather simple functions of the apparent aluminum chloride mole fraction, $\underline{N}$. The addition of a metal chloride salt results in a ternary melt, MeEtImCl-AlCl$_3$-MCl$_m$, for which the mole fraction of metal chloride salt, $\underline{N}_M$, and the stoichiometry of Equation 1, x, must be accounted for in the expressions describing Y_1 and Y_4. The new expressions are

$$Y_1 = \frac{(1 - 2\underline{N}) + (2\underline{N} - x - 1)\underline{N}_M}{(1 - \underline{N}) - (x - \underline{N})\underline{N}_M}$$

$$Y_4 = \frac{\underline{N} - \underline{N}\underline{N}_M}{(1 - \underline{N}) - (x - \underline{N})\underline{N}_M}$$

Although not used in model I, the expression for the ion fraction of the metal ion chloro complex, Y_M is

$$Y_M = \frac{\underline{N}_M}{(1 - \underline{N}) - (x - \underline{N})\underline{N}_M}$$

Noting that $Y_1 + Y_4 + Y_M = 1$, Equation 3 for model I can be expanded in terms of Y_M and Y_1 or Y_4. The alternate expression will be useful in comparing the functional form of the different models. Model I in terms of Y_M and Y_4 is

$$\delta_{obs} = (\delta_2 + \delta_8 - 2\delta_5)Y_4^2 + (2\delta_5 - 2\delta_2)Y_4 + \delta_2 + (2\delta_2 - 2\delta_5)Y_4Y_M - 2\delta_2Y_M + \delta_2Y_M^2 \quad (4)$$

Since δ_2, δ_5 and δ_8 are known,[5] the chemical shifts predicted by the model as a function of $\underline{N}_M$ may be calculated from Equation 3. Actually a family of theoretical curves are obtained according to the composition of the binary used in the experiment and a set of integer x's. An example of such a family of curves is shown in Figure 2. Also shown in this figure are δ_{obs}

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vs $\underline{N}_M$ data obtained for the MeEtImCl-AlCl$_3$-MCl$_m$ ternary melts.

The ability of model I to predict the δ_{obs} dependence on the MCl$_m$ fraction, and thus determine x of Equation 1, may be seen in Figure 2. The predicted line for each x is close to the experimental data for each system studied for small amounts of added MCl$_m$, but the data deviate significantly at higher concentrations. This simple model works surprisingly well, considering that there are no adjustable parameters other than δ_s, which was obtained from fitting the data for the MeEtImCl-AlCl$_3$ binary molt.
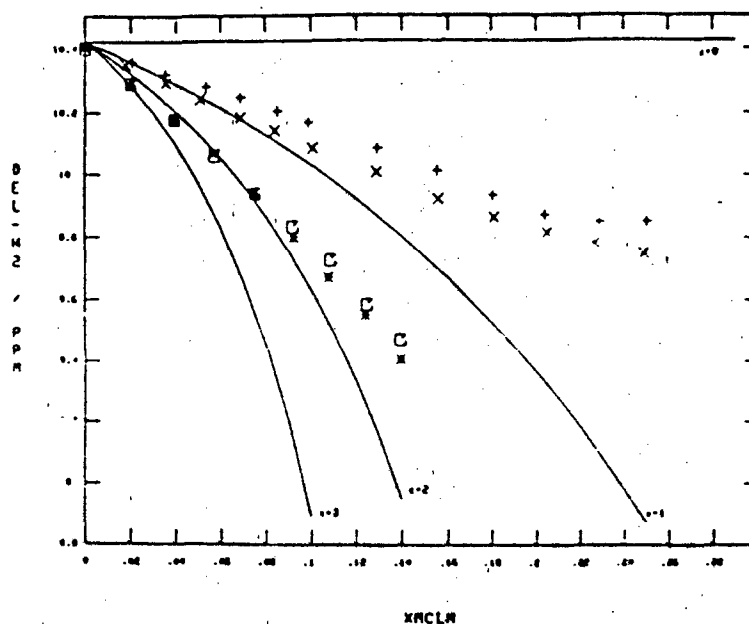

Fig. 2 Comparison of model I with experimental data. (———), model I; (+), LiCl; (X), AgCl; (*), CdCl$_2$; (□), ZnCl$_2$.

MODEL II

As can be seen from the data presented in Figure 2, Model I, while it may give a qualitative indication of x for each metal chloride salt, the actual data deviate greatly from the predicted curves. Model II attempts to ameliorate this situation as it takes into account the ion interactions between the imidazolium ions and the anionic metal chloride complexes. The imidazolium ions can now exist in six different environments as shown in Figure 3.
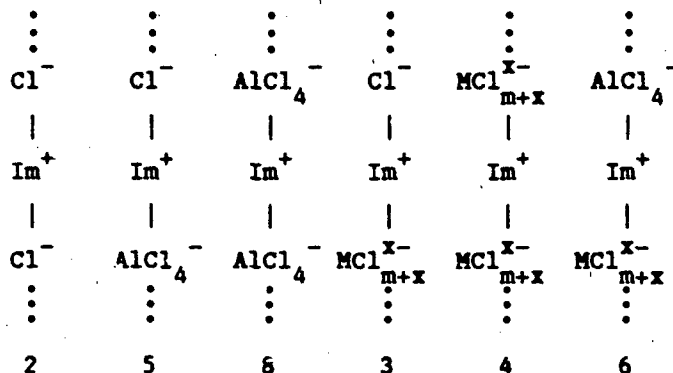
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$$
\begin{array}{cccccc}
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
Cl^- & Cl^- & AlCl_4^- & Cl^- & MCl_{m+x}^{x-} & AlCl_4^- \\
| & | & | & | & | & | \\
Im^+ & Im^+ & Im^+ & Im^+ & Im^+ & Im^+ \\
| & | & | & | & | & | \\
Cl^- & AlCl_4^- & AlCl_4^- & MCl_{m+x}^{x-} & MCl_{m+x}^{x-} & MCl_{m+x}^{x-} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
2 & 5 & 8 & 3 & 4 & 6
\end{array}
$$

Fig. 3   Ion interactions proposed by Models II and III for
MeEtImCl-AlCl$_3$-MCl$_m$ ternary melts.

The observed chemical shift is now given by Equation 5.

$$
\delta_{obs} = \delta_2 \underline{X}_2 + \delta_5 \underline{X}_5 + \delta_8 \underline{X}_8 + \delta_3 \underline{X}_3 + \delta_4 \underline{X}_4 + \delta_6 \underline{X}_6 \tag{5}
$$

Here again, the $\underline{X}_i$'s are mole fractions based on a statistical
distribution of the anions among the imidazolium environments. For this
model, the mole fractions are obtained from the multinomial distribution and
the anion fractions defined above.

$$
\begin{array}{ll}
\underline{X}_2 = Y_1^2 & \underline{X}_3 = 2Y_1 Y_m \\[8pt]
\underline{X}_5 = 2Y_1 Y_4 & X_4 = Y_m^2 \\[8pt]
\underline{X}_8 = Y_4^2 & \underline{X}_6 = 2Y_4 Y_m
\end{array}
$$

Equation 5 for model II may be expanded in terms of Y_M and Y_1 or Y_4. In
terms of Y_M and Y_4 it becomes

$$
\delta_{obs} = Y_4^2(\delta_2 - 2\delta_5 + \delta_8) + Y_4(2\delta_5 - 2\delta_2) + \delta_2 + Y_4 Y_M(2\delta_6 - 2\delta_3 + 2\delta_2 - 2\delta_5)
$$
$$
+ Y_M(2\delta_3 - 2\delta_2) + Y_M^2(\delta_2 + \delta_4 - 2\delta_3) \tag{6}
$$

Equation 6 shows that the functional form for model II is the same as for
model I, but three of the coefficients are different. Curve fitting to the
experimental data was performed with the mathematically equivalent Equation 5

Equation 5 is a linear combination of six terms. The various $\underline{X}_i$'s can

be calculated as previously discussed. The characteristic shifts of each
environment can be varied as adjustable parameters as a test of the
correctness of the various models. Used without assumption, Equation five
could be used to fit almost any data, as it contains six adjustable
parameters. However there are some simplifying assumptions which can be made
to give this model physical significance. The environments 2, 5, and 8
are exactly the same as those found in the unperturbed binary model[5],
therefore, values for δ_2, δ_5, and δ_8 are obtained from composition
dependent studies of the chemical shift of the binary MeEtImCl-AlCl$_3$ melt.

The environment 4 is that which exists in a neutral binary
MeEtImCl-metal chloride melt wherein enough metal chloride has been added to
stoichiometrically complex with all of the chloride ion provided by the
1-methyl-3-ethylimidazolium chloride (A similar assumption was made in studies
of the MeEtImCl-AlCl$_3$ binary melts for a equimolar mixture). Obviously, if
x is 1, then this would be a equimolar mixture. If x = 2, δ_4 is δ_{obs}
at N_M = 0.333, etc. That is, the value of δ_4 is dependent upon the
assumed value of x. The equimolar binary MeEtImCl-MCl$_m$ melt is generally
not experimentally obtainable due to the insolubility of the metal chloride.
However, by extrapolating data obtained for a series of less than
stoichiometric melts, an estimate for δ_4 can be otained. Data of this
type for MeEtImCl-CdCl$_2$ binaries are shown in Figure 4.

An estimate for the magnitude of δ_6 may be obtained in a similar
manner by the extrapolation of data obtained from MeEtImCl-AlCl$_3$-MCl$_m$
ternary melts at that point at which no free chloride exists in the melt, that
is, a neutral melt, if a basic melt is defined as one containing an excess of
free chloride. At this point, imidazolium ion can exist in only three
different environments (4, 6, and 8 in Figure 3). Now, δ_6 can be
calculated based on previously determined values of δ_4 and δ_8. Again,
the value of δ_6 obtained from δ_{obs} vs N_M data will depend on the
value assumed for x. Figure 5 presents data of this type for
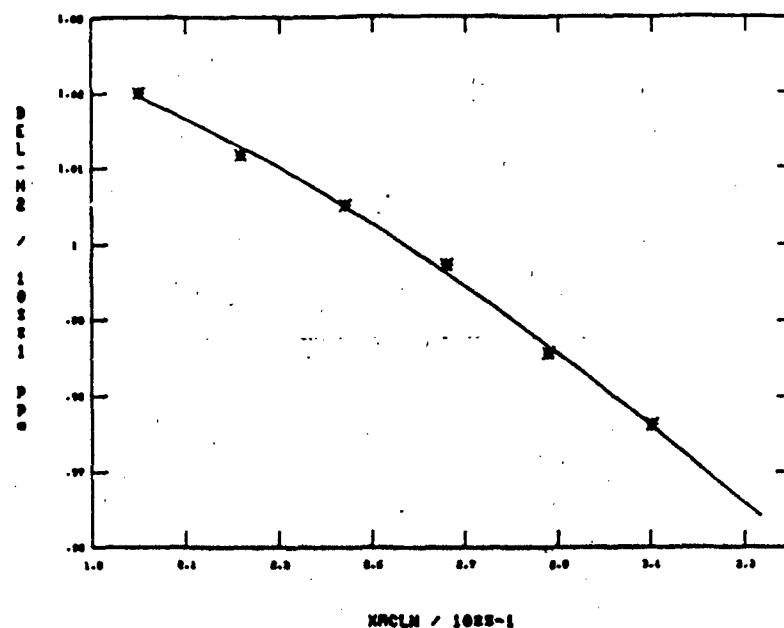MeEtImCl-AlCl$_3$-CdCl$_2$ ternary melts.

Fig. 4 δ_{obs} vs mole fraction MCl_m for MeEtImCl-CdCl$_2$ binaries at 30 °C.
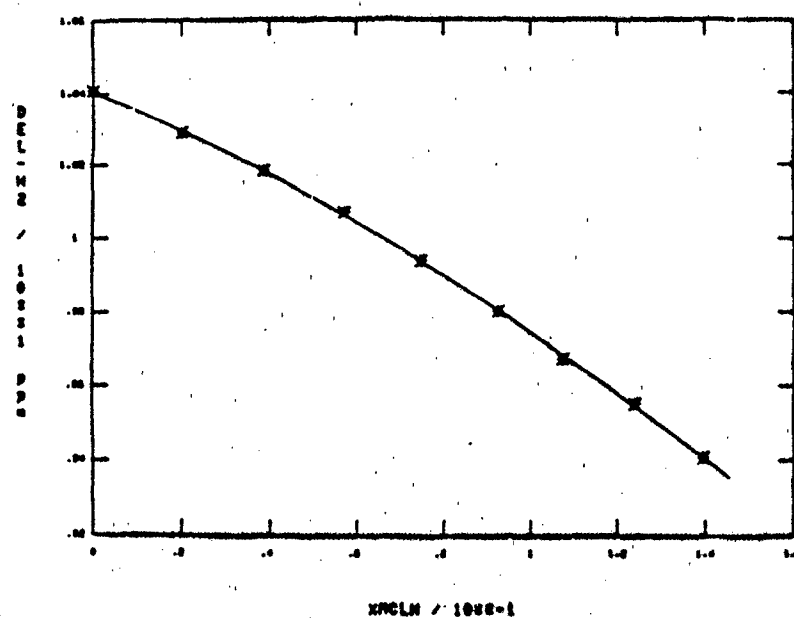
Fig. 5 δ_{obs} vs mole fraction MCl_m for MeEtImCl-AlCl$_3$-CdCl$_2$ ternaries at 30 °C.

Model II was tested in two slightly different forms. Model IIA assumed that the values obtained for δ_4 and δ_6 are correct even though they are extrapolations. Five of the six parameters in Equation 5 are now either experimentally determined or are estimated. A linearized least squares

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fitting routine was used to calculate the best value for δ_3. The results of these calculations are shown for the various metal chloride ternary melts in Figures 6-9 and Tables I-III.

As can be seen in the Figures, Model IIA fits the experimental data reasonably well, especially at low concentrations of added MCl_m. However the calculated line based on this model deviates significantly from the data at higher N_M. Model IIB allows both δ_3 and δ_6 to be adjusted by the fitting routine. The rationale for this is that the value for δ_6 was calculated based on two extrapolated values as discussed above. By examining Equation 5, it is seen that at high N_M, small errors in the values of δ_4 and δ_6 lead to large errors in the contributions of the terms involving these parameters to δ_{obs}. The theoretical lines obtained in this way fit the data very well (Figures 6-9). All of the adjusted parameters obtained by this model are reasonable estimates for the chemical shifts of the imidazolium ions in the various environments (Tables I-III).

Model II also takes into account the requirement of electroneutrality when $x >$ 1 by recognizing that the imidazolium ion has two binding sites (one on each side of the ring) and that the metal chloride complexes are large enough to complex with more than one cation. Therefore, each metal chloride complex with charge greater than one is associated with x cations, forming cross linkages between the longer ploymeric chains. Previous studies[3] have shown that the greatest chemical shift effect is wrought on each cation by its two nearest neighbors, therefore this model reduces exactly to the sitution depicted by Fig. 3. One consequence of model VI is that the viscosity of the ternary melt is increased by the cross linking of the longer chains. This is the qualitative observation for melts containing $CdCl_2$ and $ZnCl_2$.

MODEL III

Model III is an extension of Model II which attempts to simplify the situation by recognizing that at the metal chloride concentrations where the experimental data displays the greatest deviation from the simple model (Model I), there is very little free chloride left in the melt. That is, as N_M increases, Y_1 decreases. Therefore the shift contribution of the $\delta_3 X_3$ term is small and might be ignored. There are now only five environments in which the imidazolium ion exists. Equation 6 in terms of this model is given by

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Fig. 6 Comparison of the various models for MeEtImCl-AlCl$_3$-LiCl ternaries at 30 °C (– – –), model I; (• • •), model IIA; (————), model IIB, model III.

Fig. 7 Comparison of the various models for MeEtImCl-AlCl$_3$-AgCl ternaries at 30 °C (– – –), model I; (• • •), model IIA; (————), model IIB, model III.

Fig. 8 Comparison of the various models for MeEtImCl-AlCl$_3$-CdCl$_2$ ternaries at 30 °C (- - -), model I; (· · ·), model IIA; (————), model IIB, model III, model IV; (· - ·), model IV.
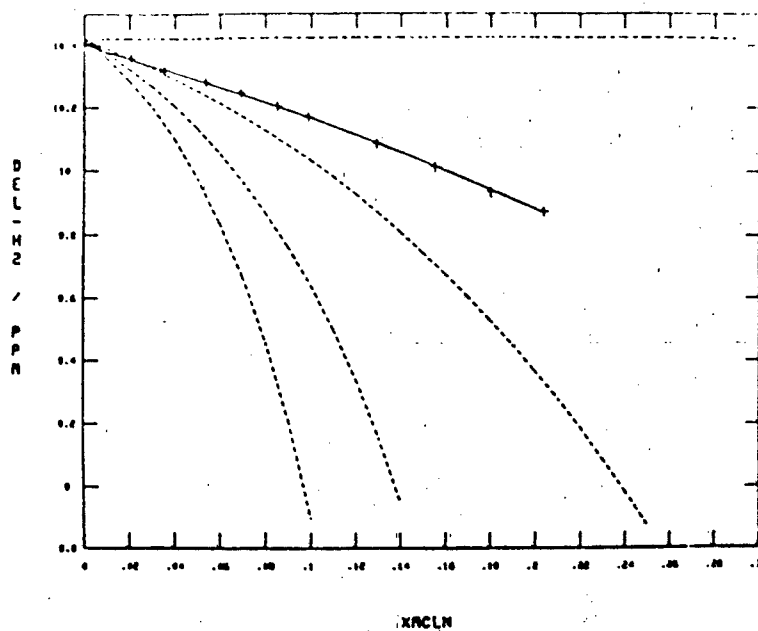

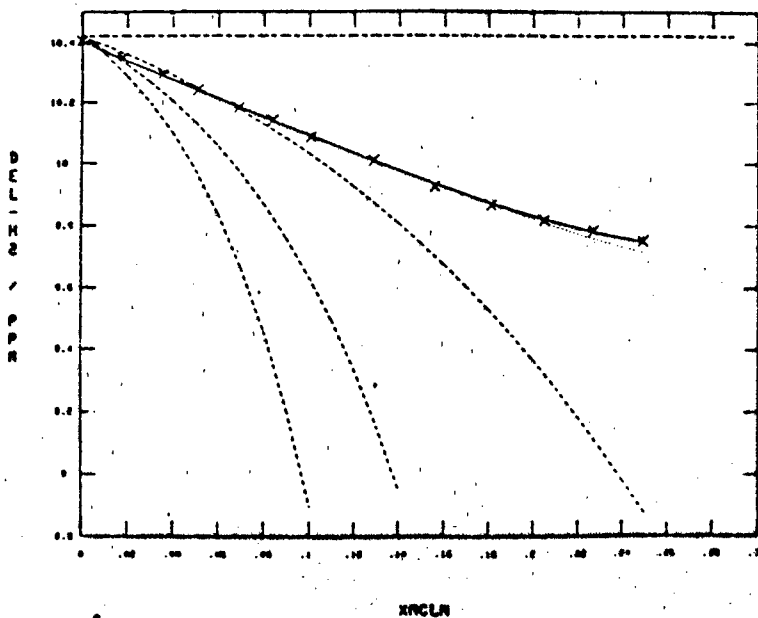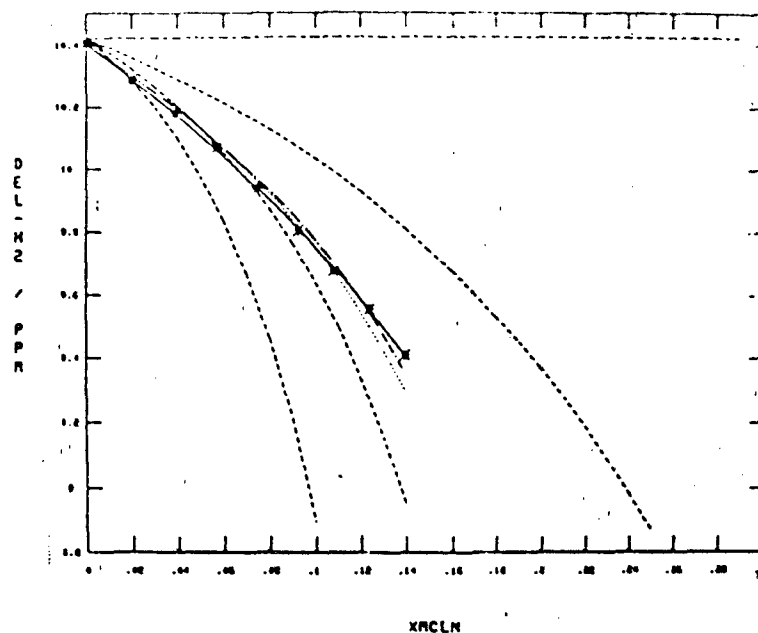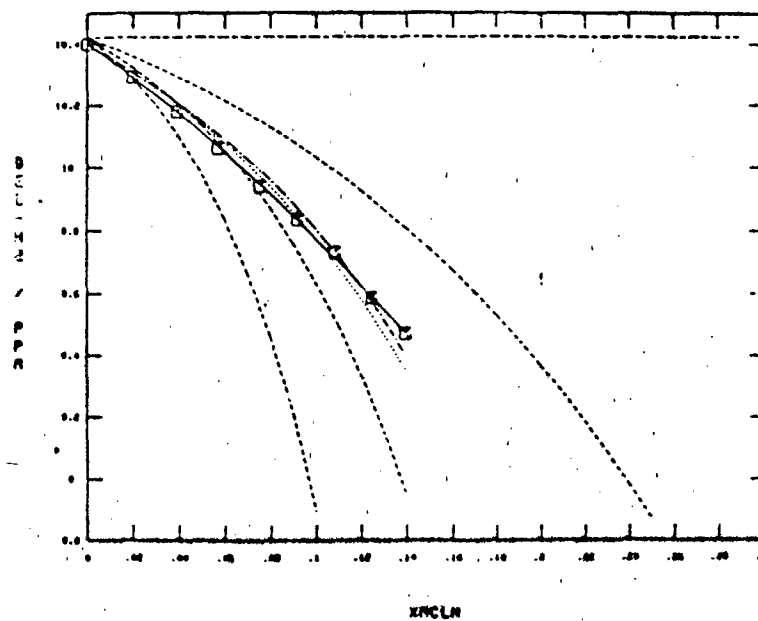
Fig. 9 Comparison of the various models for MeEtImCl-AlCl$_3$-ZnCl$_2$ ternaries at 30 °C (- - -), model I; (· · ·), model IIA; (————), model IIB, model III, model IV; (· - ·), model IV.

Table I Characteristic shift parameters for the various imidazolium environments when x = 1.

Compound	LiCl	AgCl	$CdCl_2$	$ZnCl_2$
Model				
All models				
δ_2	10.680	10.680	10.680	10.680
δ_5	11.0147[†]	11.0147[†]	11.0147[†]	11.0147[†]
δ_8	8.846	8.846	8.846	· 8.846
Model IIA				
δ_3	10.0786*	9.7655*	10.1594*	9.8153*
δ_4	9.640	10.248	8.5107	8.7656
δ_6	10.187	9.847	7.7134	8.090
Model IIB				
δ_3	10.0784*	9.5999*	10.6963*	10.0613*
δ_4	9.640	10.248	8.5107	8.7656
δ_6	10.1568*	9.9208*	7.3611*	7.9288*
Model III				
δ_4	-10.5167*	-8.9517*	-12.8818*	-11.3571*
δ_6	20.5406*	19 8116*	18.3815*	18.295*
Model IV				
δ_M is undefined for x ≠ 2.				
Model V				
δ_F is undefined for x = 1.				

[†] obtained from fits of δ_{ob} vs $\underline{N}_M$ for MeEtImCl-AlCl$_3$ binaries

* adjustable parameter

Table II Characteristic shift parameters for the various imidazolium environments when x = 2.

Compound		LiCl	AgCl	$CdCl_2$	$ZnCl_2$
Model					
All models					
	δ_2	10.680	10.680	10.680	10.680
	δ_5	11.0147[†]	11.0147[†]	11.0147[†]	11.0147[†]
	δ_8	8.846	8.846	8.846	8.846
Model IIA					
	δ_3	11.0251*	11.2147*	10.0588*	9.9909*
	δ_4	10.3714	10.4104	9.642	9.6662
	δ_6	10.4752	10.3007	9.468	9.6039
Model IIB					
	δ_3	10.0904*	9.6313*	9.2203*	9.0612*
	δ_4	10.3714	10.4104	9.642	9.6662
	δ_6	11.1187*	10.9575*	9.7714*	9.9391*
Model III					
	δ_4	−29.9902*	−28.1148*	−27.2392*	−26.5784*
	δ_6	21.5149*	20.8807*	19.2711*	19.2748*
Model IV					
	δ_M	9.6423*	9.4625*	9.686*	9.7946*
Model V					
	δ_3	10.2154*	9.8008*	10.1131*	9.8308*
	δ_5	11.0147[†]	11.0147[†]	11.0147[†]	11.0147[†]
	δ_8	8.846	8.846	8.846	8.846
	δ_F	10.876*	10.8064*	9.7383*	9.8564*

[†] obtained from fits of δ_{obs} vs N_M for MeEtImCl-AlCl$_3$ binaries

* adjustable parameter

Table III   Characteristic shift parameters for the various imidazolium environments when x = 3.

Compound	LiCl	AgCl	$CdCl_2$	$ZnCl_2$
Model				
All models				
δ_2	10.680	10.680	10.680	10.680
δ_5	11.0147[†]	11.0147[†]	11.0147[†]	11.0147[†]
δ_8	8.846	8.846	8.846	8.846
Model IIA				
δ_3	14.0471*	14.6145*	11.8985*	11.7502*
δ_4	10.370?	10.4914	10.0252	10.0091
δ_6	10.7112	10.0838	10.0262	10.0961
Model IIB				
δ_3	10.1153*	9.7924*	9.1529*	8.8286*
δ_4	10.3702	10.4914	10.0252	10.0091
δ_6	12.0437*	11.8197*	10.9602*	110.859*
Model III				
δ_4	−50.3214*	−48.263*	−44.892*	−42.9625*
δ_6	22.4655*	21.9088*	20.3905*	20.182*
Model IV				
δ_M is undefined for x ≠ 2.				
Model V				
δ_3	9.8634*	9.4434*	9.9389*	9.4843*
δ_4	10.3702	10.4914	10.0252	10.0091
δ_6	10.7112	10.0838	10.0262	10.0961
δ_F	11.148*	11.370*	10.4025*	10.4742*

[†] obtained from fits of δ_{obs} vs $\underline{N}_M$ for MeEtImCl-AlCl$_3$ binaries

* adjustable parameter

$$\delta_{obs} = Y_4^2(\delta_2 - 2\delta_5 + \delta_8) + Y_4(2\delta_5 - 2\delta_2) + \delta_2 + Y_4 Y_M(2\delta_6 - 2\delta_5 + 2\delta_2)$$

$$- Y_M(2\delta_2) + Y_M^2(\delta_4 + \delta_2) \tag{7}$$

The experimental data was also fit to this model to test its validity. These results are presented in Figures 6-9. The fit to the data is excellent, but examination of the adjusted values of δ_4 and δ_6 (Tables I - III) shows that they are not physically meaningful, therefore, model II is better.

MODEL IV

This model attempts to explain the observed chemical shift dependence in a somewhat different manner. The different imidazolium environments can be pictured as shown in Figure 10.
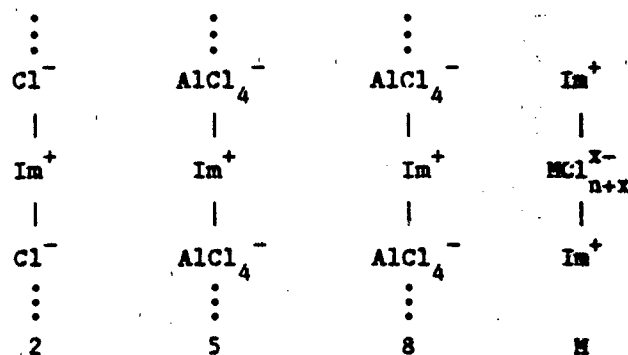

Fig. 10 Ion interactions proposed by Model IV.

This model is similar to the previous three in that environments 2, 5, and 8 are present. However, it introduces a fourth environment, denoted by M, which differs significantly from previously defined environments. Environment M is postulated to not take part in the long chain associations[3] as do the others. Equation 3 in terms of this model is

$$\delta_{obs} = \delta_2 X_2 + \delta_5 X_5 + \delta_8 X_8 + \delta_M X_M \tag{8}$$

The mole fractions of environments 2, 5, and 8 are defined differently than in the previous discussion. This model requires that a certain fraction of the total moles of imidazolium no longer take part in the statistical distribution among the various pairs of anions present in the melt. The mathematical situation is exactly that which would result if environment M

were an isolable species. That fraction of the total moles of imidazolium ion which is involved in environment M is given by

$$X_{Imc} = \frac{2N_M}{(1-\underline{N})(1-N_M)}$$

The fraction of imidazolium which is involved in the long chain associations is

$$X_{Ims} = 1 - X_{Imc}$$

Another effect of the postulation of M is the decrease in the number of moles of ImCl which is available to the environments 2, 5, and 8 by an amount equal to twice the number of moles of MCl_m added to the melt. Therefore the anion fractions of Cl^- (Y_1) and $AlCl_4^-$ (Y_4) are now given by

$$Y_1' = \frac{(1-2\underline{N}) - (3-2\underline{N})N_M}{(1-\underline{N}) - (3-\underline{N})N_M}$$

$$Y_4' = \frac{\underline{N}(1-N_M)}{(1-\underline{N}) - (3-\underline{N})N_M}$$

The mole fractions of environments 2, 5, 8, and M in Equation 8 are given by

$$\underline{X}_2 = (Y_1')^2 X_{Ims} \qquad\qquad \underline{X}_4 = 2Y_1'Y_4'X_{Ims}$$

$$\underline{X}_8 = (Y_4')^2 X_{Ims} \qquad\qquad \underline{X}_M = X_{Imc}$$

As the various $\underline{X}_i$'s are defined differently than in the previous models, Equation 8 can no longer be expanded into an equation involving only Y_1, Y_4, and Y_M (ie., similar to Equation 5). Therefore, a direct mathematical comparison of model IV with previous models is not possible. This model was tested for its ability to explain the experimental observations. Theoretical lines calculated based on this model are also included in Figures 8 and 9. When δ_M is the only adjustable parameter, Equation 8 does give a reasonable representation of the experimental data (Figures 8 & 9). Note that

this model is undefined for $x \neq 2$.

<u>MODEL V</u>

Model V is an alternative to model IV which meets the requirement of electroneutrality when x is greater than one. In this situation (as is always the case when $x \neq 1$), because of the complexation of chloride ions from the melt by the added metal chloride, the number of anions is now less than the number of cations, even though the number of charges remain equal. Model V postulates that the excess cations associate with the metal chloride complexes in a different way than those involved in the long chain interactions, as illustrated in Figure 11.

$$\vdots$$
$$MCl_{m+2}^{2-}[Im^+] \qquad MCl_{m+3}^{3-}[2Im^+]$$
$$| \qquad\qquad\qquad |$$
$$Im^+ \qquad\qquad\qquad Im^+$$
$$| \qquad\qquad\qquad |$$
$$(\quad)^- \qquad\qquad (\quad)^-$$
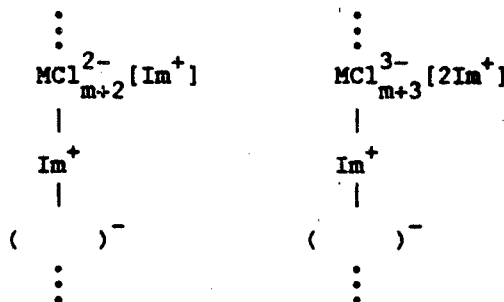$$\vdots \qquad\qquad\qquad \vdots$$

Fig. 11 Ion interactions proposed by Model V.

In addition to the two environments depicted here, all of the imidazolium environments included in model II are also present. The other anion involved in the polymeric association can be any one of the other anions present in the melt, therefore, there are three slightly different imidazolium environments described by this model for each value of x greater than one. However, this model holds that the major chemical shift effects are derived from the close association of the free or excess cations with the metal chloride complex, so that all of the free cations experience essentially the same environment. The free imidazolium environment (denoted by F) is given by

$$\underline{X}_F = \frac{(x-1)\underline{N}_M}{(1-\underline{N})(1-\underline{N}_M)}$$
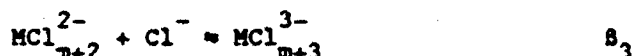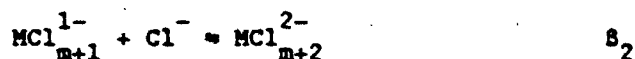
Note that according to model V, the free imidazolium cation is associated with an anion at only one of its binding sites (<u>vide</u> <u>supra</u>). The observed chemical shift is given by

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$$\delta_{obs} = \delta_2 X_2 + \delta_5 X_5 + \delta_8 X_8 + \delta_3 X_3 \, \delta_4 X_4 + \delta_6 X_6 + \delta_F X_F \qquad (9)$$

The anion fractions, Y_1, Y_4, and Y_M are calculated exactly as in model II. However, as in model IV, the various mole fractions must be multiplied by that fraction of imidazolium which takes part in the long chain associations (ie., $X_{Ims} = 1-X_F$), therefore, the derivation of an equation similar to Equation 5 is not possible. This model was also tested as to its ability to explain the experimental data, allowing δ_3 and δ_F to vary as adjustable parameters. Equation 9 can be made to fit the data quite well and the values returned for δ_3 and δ_F are reasonable (Figures 8 & 9 and Tables I-III). Note, however, that model V reduces to model II when $x = 1$. Application of Occam's razor indicates that model II is therefore superior to model V.

MODEL VI

Model VI assumes the stepwise formation of several different metal chloro complexes when MCl_m is added to the melt according to

$$MCl_m + Cl^- \rightleftharpoons MCl_{m+1}^{1-} \qquad\qquad \beta_1$$

$$MCl_{m+1}^{1-} + Cl^- \rightleftharpoons MCl_{m+2}^{2-} \qquad\qquad \beta_2$$

$$MCl_{m+2}^{2-} + Cl^- \rightleftharpoons MCl_{m+3}^{3-} \qquad\qquad \beta_3$$

$$MCl_m + 3Cl^- \rightleftharpoons MCl_{m+3}^{3-} \qquad\qquad K = \beta_1\beta_2\beta_3$$

where the β_i's are stepwise formation constants. There are now as many as fifteen different imidazolium environments to consider, each with its own characteristic chemical shift. By the techniques already described it is possible to measure or estimate five of the fifteen δ's. However, none of the mole fractions are available since the value of x is now non-integer. Equation 5 for this model has 25 unknowns.

There are some simplifying assumptions which make this model tenable, howver. Recognizing that metal chloride complexes of this type are large and, therefore have low charge densities, the effect upon the cation would be approximately the same for all possible combinations of cations and anions.

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Now, the characteristic chemical shifts of the six environments involving two metal chloride complexes is approximated by δ_4 of model II. In a like manner, the various combinations of a metal chloride complex and a melt anion are approximated by δ_3 and δ_6. Also recognizing that as long as the value of K for the overall formation reaction is 10 or greater (which has been observed by potentiometric titrations of ternary chloroaluminate melts containing metal chloride salts[7]), only one of the possible metal chloride complexes would predominate. Therefore, this model also reduces to model II.

Conclusion

From a comparison of all of the data presented in Figures 6-9 and Tables I-III, it is clear that of all of the models tested, model IIB is the best at explaining the experimental data. This method can be used to determine x for a given ternary molten salt system under conditions which are greatly different than the normal method of potentiometric titration, that is, high metal chloride salt concentrations. It has the additional advantage of allowing insight to be gained into the physical structure of ternary melts.

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